Hydrogen Bonds in Dilute Solutions of Poly(ethylene glycol)

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ABSTRACT: The hydrogen bond in dilute solutions of different poly(ethylene glycol) monodisperse fractions with molecular weights from 300 to 6000 has been studied in carbon tetrachloride by IR spectroscopy using a computer for spectrum resolution. The dependences of the equilibrium constants on the polymer molecular weight have been determined for different forms of intra- and intermolecular hydrogen bonds.

Introduction

The formation of hydrogen bonds (HBs) due to the interaction between donor and acceptor functional groups, simultaneously existing in a macromolecule, is characteristic of many heterochain polymers. A typical representative of these polymers is poly(ethylene glycol) (PEG). The end hydroxyls of the latter form both intra- and intermolecular H complexes with the ether oxygens of the main chain. This phenomenon might be the reason for some anomalies in the behavior of polymers in dilute solutions. For example, for PEG solutions in benzene an unusual dependence of the second virial coefficient A_2 on the polymer chain length is observed. It is exhibited by a change in the A_2 sign from a positive value to a negative one when the molecular weight is descreased.[1] The dependence of the reactivity of PEG hydroxyl groups on the PEG degree of polymerization (found in the reaction with isocyanate in some solvents) is one more interesting phenomenon related to complexation of end hydroxyls with oxygen atoms of the main chain.[2-4] An appreciable deviation from the Flory principle is also found during benzoylation of polyarylates containing end hydroxyl groups.[5,6] The common reason is the presence of several forms of H complexes with different reactivities in the solution. The ratio between them depends on the molecular weight and the solution concentration.

Experimental Section

Materials. PEGs with molecular weights lower than 1000 were dried for 6 h at 60 °C under vacuum over phosphoric anhydride. PEGs with higher molecular weights were used without a preliminary purification. The average molecular weight, $\bar{M}_n$, of PEG was determined from the total content of hydroxyl groups in IR spectra of polymer solutions in tetrahydrofuran (THF) by the procedure described in ref 7. The obtained values of $\bar{M}_n$ are listed in Table I. For all PEGs the width of molecular weight distribution ($\bar{M}_w/\bar{M}_n$) determined by GPC does not exceed 1.1.

Ethylene glycol monomethyl ether (EME) was distilled at 124 °C. Diethyl ether (DE) was purified as described in ref 8. Chemically pure commercial THF was dried for 2 days over potassium hydroxide and then twice distilled over lithium aluminum hydride in an argon flow; fractions with the boiling point of 65 °C were selected. CCl_4 distilled over phosphoric anhydride (bp 76 °C) was used as a solvent.

Measurements of IR Spectra and Their Resolution. IR spectra of PEG solutions were recorded with a UR-20 spectrophotometer, with a LiF prism over the range from 3100 to 3900 cm^{-1} at 30 °C. For PEG solutions with the concentration $5 \times 10^{-3} - 10^{-2}$ mol/L, cells with path lengths of 0.36 cm were used and for solutions with the concentration $2 \times 10^{-4} - 8 \times 10^{-4}$ mol/L those with path lengths of 4.4 cm. IR spectra were resolved to isolate individual absorption bands (Figure 1). Most of the available methods of spectrum resolution are based on an assumption of the definite character (for example, Gaussian or Lorentz) of each partial band in the spectrum. Therefore, first of all shapes of individual bands were determined. It has been shown that in the spectra of PEG (with the molecular weight higher than 3000) solutions in CCl_4, consisting of two bands with maxima at 3610 and 3510 cm^{-1}, the overlapping free long-wave region of the band at 3510 cm^{-1} is well described by a Gaussian function (Figure 1b). Simultaneously it has been found in EME dilute solutions in CCl_4 that the band at 3610 cm^{-1} is of Lorentz shape, in agreement with the published data.[9,10] The form of the spectrum $F(x)$ was simulated by a sum of three components with different values of the band position x_i, half-band width Δ_i, and optical density D_i. The values of parameters (x_i, Δ_i, D_i) fitting best the appropriate experimental data were determined with a BESM-6 computer using a packet of programs for the analysis of badly resolved spectra.[11,12] The possibility of representation of the spectrum form for stretching vibrations of OH groups, participating in the formation of weak HBs, by a sum of Gaussian curves is theoretically substantiated.[13] When a great number of individual bands in the spectrum are given, the main peaks shown in Figure 1 retain their parameters, but the confidence ranges of each of the quantities x_i, Δ_i, and D_i are greatly enhanced. The good agreement between the model and the experiment and the known shapes of individual bands permit one to draw a conclusion on the adequacy of the model used.

Table I
$\bar{M}_n$ of the PEG Samples

PEG samples	firm	$\bar{M}_n$
300	"Loba chemie" Austria	290
600	"Loba chemie" Austria	510
1000	"Merck-Schuchardt" GFR	920
3000	"Schuchardt-München" GFR	2860
6000	"Loba chemie" Austria	6020

Theoretical Calculations of the Constants of the Formation of Intramolecular HBs. The Monte Carlo method is used to simulate self-avoiding polymer chains using a BESM-6 computer. Each group of chains (O or CH_2) is simulated by a rigid sphere. The Morse potential is introduced for taking into account the intramolecular HBs between the end hydrogen atom and oxygen atoms of the main chain. By averaging 500–4000 chain configurations, the mean local density of oxygen atoms near the OH group and the concentration of intramolecular rings of different sizes are determined.

Osmometry. Measurements were carried out by using a gas osmometer, similar to that described in ref 14, in PEG solutions in CCl_4 with the concentration lower than 8 g/dL at 30.2 °C.

Results and Discussion

Attribution of Absorption Bands of Hydroxyl Groups. Since the purpose of this investigation was to study HBs, the authors used absorption bands of OH-group stretching vibrations, because these groups are most sensitive to HB formation. The small band structures in the region 3300–3800 cm^{-1} cannot arise from Fermi resonance interactions with overtones of lower lying vibrational bands, since the corresponding bands must be found in a lower frequency region of the spectrum ($\nu < 3000$–3300 cm^{-1}).[15] According to the literature data,[15] they have a characteristic shape, essentially different from those obtained in the present study (Figure 1).

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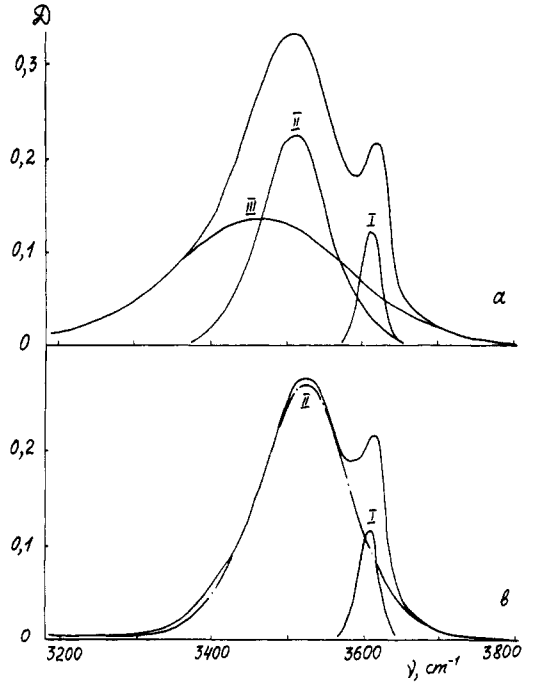


Figure 1. IR spectra of PEG with molecular weight 1000 (a) and 3000 (b) in CCl_4, resolved into individual bands, obtained with a computer ($C_{PEG} = 8 \times 10^{-3}$ mol/L).

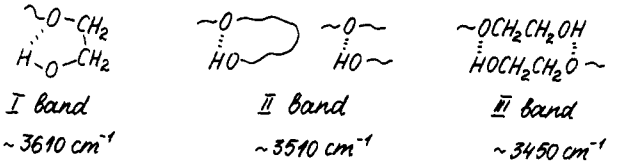


Figure 2. H complexes in dilute solutions of PEG in CCl_4.

Resolution of the spectrum into individual components permits one, as a rule, to separate three absorption bands in the range of stretching vibrations of the hydroxyl group: at ~3610, ~3510, and ~3450 cm^{-1} (Figure 1). The band corresponding to absorption of a free OH group at 3640 cm^{-1} is absent in the studied PEG spectra.

The first absorption band at ~3610 cm^{-1} is attributed to vibrations of the hydroxyl group intramolecularly bound to a five-membered ring[2,10,16] (Figure 2). The second band at ~3510 cm^{-1} is due to vibrations of OH groups bound to the ether oxygen atoms, both intermolecularly and intramolecularly in large rings of any size, containing more than five members[2] (Figure 2). OH groups participating in the formation of HBs of the type OH···OH in dimers can absorb in the same spectrum region.[17] This type of absorption by bound OH groups, however, can be neglected under our conditions, since we have worked with sufficiently low concentrations of PEG solutions. It has been shown with low molecular weight alcohols[17] that at these concentrations dimer associates with HBs of the type OH···OH are not formed. Probably the third band at ~3450 cm^{-1} can be attributed to the stretching vibrations of OH groups bound by intra- or intermolecular HBs in a 10-membered ring (Figure 2). It follows from the analysis of the spectra of model compounds: ethylene glycol and diethylene glycol monoethers.[10] HBs in the 10-membered ring are stronger than single HBs of the type OH···OH; therefore, dimer associates appear in this case at such a low concentration of PEG[10] when single HBs are practically not yet formed.

It has been shown that the spectral characteristics of the first band (the position of a maximum and half-width)

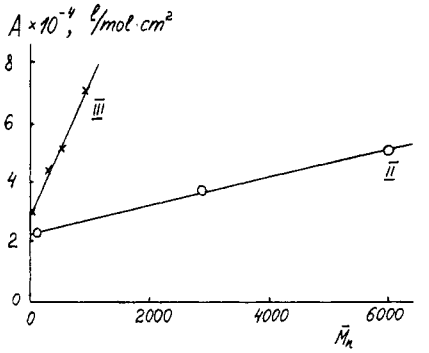


Figure 3. Dependence of the integral extinction coefficients of bands II and III on molecular weight of PEG.

Table II
Constants of HB Formation according to Reactions 2, 3, and 7

PEG mol wt	K_2	K_3	$10^{-3}K_6$, L/mol
200	0.37		1.35
300	0.50	0.50	1.35
600	0.70	0.30	1.35
1000	0.90	0.15	1.25
3000	1.20		
6000	1.25		

practically depend neither on molecular weight nor on the PEG solution concentration (Table II). As to the second band, it is slightly broadened and its maximum is shifted toward higher frequencies, both with an increase in the PEG molecular weight and with an increase in the concentration of its solution (Table II). For the third band an increase in molecular weight and in the PEG solution concentration results in band broadening (Table II). For PEG with molecular weight higher than ~2000 this band has not been observed in the studied concentration range (Table II).

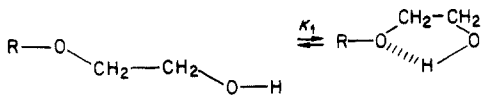
Since the spectral characteristics of the first band depend neither on PEG molecular weight nor on its concentration in the solution, we assume that the integral extinction coefficient of this band, A_I, remains constant for different molecular weights and equals 0.64×10^4 L/(mol·cm²), i.e., to the same value as for the model compound—ethylene glycol monomethyl ether (EME).[16] Then for PEG solutions with molecular weight higher than ~2000 with the spectrum containing only two bands, I and II, it is possible, using the value of A_I, to determine the integral extinction coefficient for the second band A_{II}. It is found to be constant for different concentrations of PEG with a given molecular weight, but it linearly increases with the increasing polymer molecular weight (Figure 3) that can be caused by different extinction coefficients of OH groups both in intramolecular rings of different dimensions and in intermolecular associates contributing to the spectrum band II (Figure 2). The first point on straight line II in Figure 3 corresponds to the extinction coefficient of the considered band in the solution of diethylene glycol monomethyl ether.[10] The extrapolation of this straight line for small molecular weight permits one to obtain the values of A_{II} for these polymers for which all three absorption bands are found in the spectra at any concentrations of the solution. A_{III} can be determined by the known values of the integral extinction coefficients for the first two bands. This coefficient is also constant for different concentrations of PEG with a given molecular weight, but it linearly increases with increasing molecular weight (Figure 3). The extinction coefficients thus observed permit one to determine the concentration of each form of the OH-group complex and to calculate the equilibrium constants

for the reactions of the formation of different HBs.

HBs in Model Systems. Hydrogen bonds in PEG molecules result from the interaction between the end hydroxyl groups and ether oxygens of the main chain. Their characteristics can be affected by factors of two types: (1) the effect of the immediately adjacent units of the considered functional group, (2) the long-range order effect related to molecule fragments located relatively far from the functional group along the polymer chain, but at a small distance in space, due to favorable conformations of the molecule.

To take into account the short-range order effects it suffices to study HBs between two corresponding low molecular weight model substances, one of which contains a hydroxyl group and the second an ether group. We have chosen EME and diethyl ether (DE) as models of end and internal fragments of PEG. To avoid the EME self-association, its concentration in the CCl_4 solution did not exceed 10^{-2} mol/L and DE concentration was by 2 orders of magnitude higher.

The spectrum of a dilute EME solution in the region of OH-group stretching vibrations exhibits two bands: 3612 and 3645 cm^{-1}, which are attributed to the absorption by OH groups intramolecularly bound in a five-membered ring and free OH groups, respectively.[16,18] In solutions these two forms of EME molecules are in a state of equilibrium:



$$K_1 = \frac{C_I}{C_F} \quad (1)$$

The equilibrium constant, K_1, is 0.09 and practically does not depend on the R nature in the series CH_3, C_2H_5, C_4H_7, $CH_3OCH_2CH_2$, $C_2H_5OCH_2CH_2$.[10,16] It is natural to assume that K_1 has also the same value for PEG. Then it is possible to calculate the concentration, C_F, of free OH groups in the polymer by using the known concentration of five-membered rings, since C_F is so small that it cannot be determined with sufficient accuracy directly from PEG spectra.

When DE is added to the EME solution, one more band appears in the spectrum at 3490 cm^{-1} due to the absorption of OH groups participating in the formation of intermolecular HBs with ether. We have calculated the constant of the HB formation in EME–DE using the formula $K_M = [OH\cdots O]/[OH][O]$; it is found to be equal to 5.8 ± 0.4 L/mol at 30 °C. Let us mention for comparison that the corresponding constant of the HB formation in ethanol–DE is 0.79 L/mol.[19] The difference in the values of the constants is, evidently, due to EME (pK_a = 14.8[20]) having appreciably more acidic properties as compared to ethanol (pK_a = 15.9[20]), because of the inductive effect of methoxy groups. It is interesting to elucidate how the polymeric nature of the carrier of the functional group affects the HB characteristics. With this purpose HB has been studied in a simpler system where one of the functional groups OH and O is in the macromolecule, while the other belongs to the low molecular weight substance.

We have chosen a system in which PEG was a hydroxyl-containing component and DE was a low molecular weight base. Ether being a poor solvent for PEG, in these experiments we have used a polymer with low molecular weight (1000) and an ether concentration not higher than 4.2 mol/L. The spectrum of the initial PEG solution consists of three bands (Figure 1, Table II). The addition of DE does not result in the formation of a new absorption band; it only causes the redistribution of the intensities of the available bands (Figure 4). The linear increase in

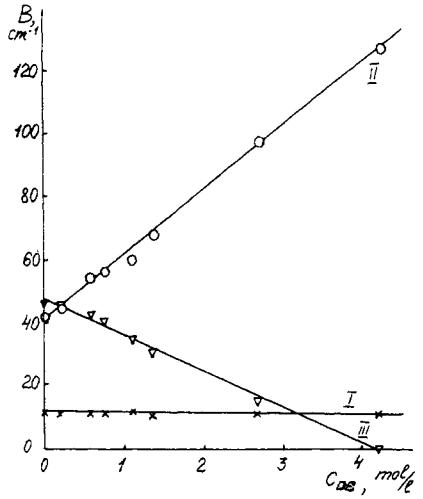


Figure 4. Dependence of the integral intensity of bands I–III in solution of PEG with molecular weight 1000 ($C_{PEG} = 5 \times 10^{-3}$ mol/L) on the concentration of the added DE.

the optical density of the second band with the increasing ether concentration shows that HBs are formed mainly between OH groups of PEG and DE.

$$B_{II} = A_{II}^{PEG} l C_{II}^{PEG} + A_{II}^{DE} l C_{II}^{DE} = A_{II}^{PEG} l C_{II}^{PEG} + A_{II}^{DE} l K C_F C_{DE}$$

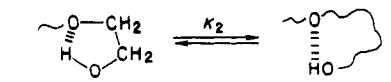
From the slope of the straight line we can calculate the constant of the formation of intermolecular HBs in the system PEG (molecular weight 1000) – DE

$$K = C_{II}^{DE}/C_F C_{DE}$$

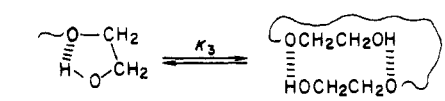
where C_{II}^{DE} is the concentration of PEG OH groups participating in the formation of HBs with DE, C_F is the concentration of the free OH groups, and C_{DE} is the concentration of DE.

The constant K is 5.0 L/mol and its value is close to that of the corresponding constant of the HB formation in the low molecular weight model system EME–DE which equals 5.8 L/mol. Thus, a conclusion can be drawn that EME is a sufficiently good model of the end of the PEG polymer chain.

Intramolecular Hydrogen Bonds in PEG. Let us consider the simplest case for studying HBs in PEG, viz., intramolecular HBs. To exclude completely the contribution of intermolecular interactions, the ratios of the band integral intensities have been extrapolated to the solution zero concentration (Figure 5). That permits one to find the values of the ratio of concentrations of the respective intramolecular HBs. It is obvious that these values are the equilibrium constants of the monomolecular reactions:



$$K_2 = \frac{C_{II\ (intra)}}{C_I} \quad (2)$$



$$K_3 = \frac{C_{III\ (intra)}}{C_I} \quad (3)$$

First we consider equilibrium 2. Since the absorption band II of PEG spectra is contributed to by OH groups participating in the formation of intramolecular rings of any dimensions with the number of members l more than 5, K_2 is the overall constant $K_2 = \sum_{l>5} K_l = \sum_{l>5} C_l/C_5$. The values of the constant K_2 for PEG with different molecular weights are represented in Table III. It is seen that the values of K_2 increase with the increasing length of the polymer chain; they reach their ultimate value for PEG

Table III
Parameters of the OH-Group Absorption Bands in Spectra of Solutions of PEG with Different Molecular Weights and of Different Concentrations

	4×10^{-4} M PEG						8×10^{-3} M PEG					
	I band		II band		III band		I band		II band		III band	
mol wt	ν, cm^{-1}	$\Delta\nu_{1/2}$, cm^{-1}	ν, cm^{-1}	$\Delta\nu_{1/2}$, cm^{-1}	ν, cm^{-1}	$\Delta\nu_{1/2}$, cm^{-1}	ν, cm^{-1}	$\Delta\nu_{1/2}$, cm^{-1}	ν, cm^{-1}	$\Delta\nu_{1/2}$, cm^{-1}	ν, cm^{-1}	$\Delta\nu_{1/2}$, cm^{-1}
300	3610 ± 1	32 ± 4	3505 ± 4	105 ± 8	3452 ± 9	198 ± 6	3610 ± 1	32 ± 2	3504 ± 4	111 ± 9	3442 ± 18	235 ± 11
600	3610 ± 1	32 ± 2	3506 ± 6	110 ± 7	3448 ± 12	216 ± 11	3610 ± 1	32 ± 2	3513 ± 2	118 ± 5	3435 ± 18	245 ± 11
1000	3609 ± 1	32 ± 2	3511 ± 2	110 ± 7	3453 ± 14	221 ± 12	3609 ± 1	32 ± 3	3514 ± 2	118 ± 4	3444 ± 14	245 ± 10
3000	3610 ± 2	32 ± 3	3512 ± 3	130 ± 4			3610 ± 1	32 ± 3	3518 ± 2	145 ± 5		
6000	3609 ± 2	32 ± 4	3519 ± 4	141 ● 5			3610 ± 2	32 ± 4	3524 ± 3	150 ± 6		

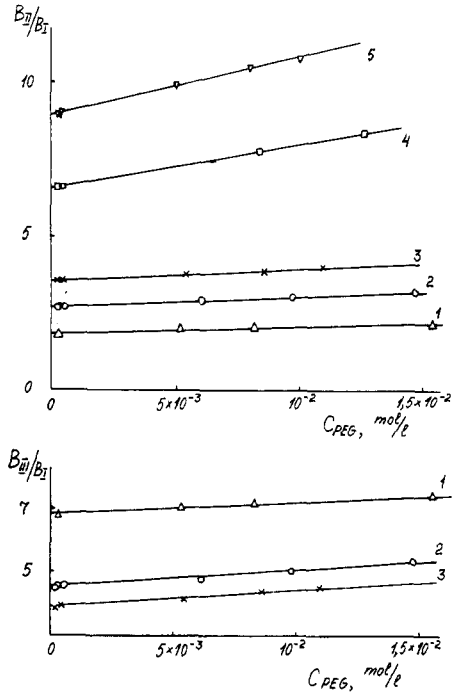


Figure 5. Dependence of the ratio of the band integral intensities on the total concentration of solutions of PEG with different molecular weights: (1) 300, (2) 600, (3) 1000, (4) 3000, (5) 6000.

with molecular weight higher than 2000. To explain this regularity the effective concentration of the ether groups should be introduced. For the HB formation, an ether oxygen atom of the main chain must approach, because of the thermal motion of the macromolecule, the end OH group. The equilibrium concentration for such oxygen atoms, C_{eff}, can be determined, according to the law of mass action, from the formula

$$C_{eff} = C_B/C_F K_4 \quad (4)$$

Here C_B and C_F are the concentrations of "bound" and "free" hydroxyl groups, respectively, and K_4 is the constant of the HB OH···O formation; the latter is assumed to be independent of the position of an oxygen atom in the chain and equal to K_M for the model system EME–DE. Since the band corresponding to absorption of free hydroxyl groups is not seen in IR spectra of PEG solutions, it is more convenient to consider C_{eff} for different forms of HBs with respect to C_{eff} for the five-membered ring equal, according to eq 4 and 1, to $1/K_I K_M$. In particular, the HBs in rings with the number of members $l > 5$

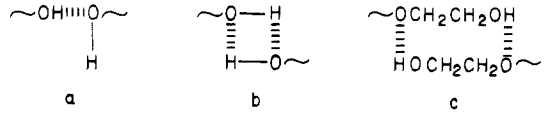
$$C_{eff} = K_2(l)/K_I K_M \quad (5)$$

Since K_I and K_M remain constant when PEG molecular weight is varied, the dependence $K_2(l)$ is the same as $C_{eff}(l)$.

Taking the data of IR spectroscopy for K_2 determination and using formula 5, the values of C_{eff} for different molecular weights of the polymer have been found. The theoretical calculations, made with the rotational-isomeric model of the PEG molecule and the known values of bond length, valent angles, and the potentials of internal rotation,[21] predict the $C_{eff}(l)$ dependence correlating well with the experimental dependence (Figure 6). This course of the $C_{eff}(l)$ curve is due to the additive contributions to the C_{eff} value of oxygen atoms separated from the end group by different numbers of units. The relative contribution of each oxygen atom decreases with the increasing distance from the chain end. That results in the value of C_{eff} leveling off.

Let us consider equilibrium 3. A dramatic drop of the constant K_3 with the increasing molecular weight of PEG (Table III) seems to indicate that this H complex is formed as a result of the end-group interaction. With the increasing length of the polymer chain, the probability of interaction of the chain end groups becomes smaller because of considerable entropy losses caused by a depletion of the macromolecule conformation set at the transition from the linear form to the ring form, according to reaction 3.

At the interaction of the end groups three types of structures may be formed



a is less favorable energetically in comparison to b and c because of a smaller value of the enthalpy change, ΔH, at its formation. That is confirmed by a smaller value of the frequency shift $\Delta\nu$ of the corresponding bands in the IR spectrum.[17] b may be excluded because of a considerable strain of the four-membered ring.[10] Thus, the most probable interaction of the end groups of the polymer chain is the formation of 10-membered ring, i.e., c. Larger rings are less favorable because of appreciable losses in the entropy, ΔS, at their formation.

Intermolecular Hydrogen Bonds in PEG. Intermolecular HBs lead to an association of macromolecules and appreciably affect the thermodynamic quality of the solvent.

In the studied range of PEG concentrations in solutions two forms of intermolecular HBs can be found (Figure 2). The first is formed according to the scheme

$$\sim OH + \sim O\sim \overset{K_5}{\rightleftharpoons} \sim OH\cdots O\sim \qquad K_5 = \frac{C_{II(inter)}}{C_F C_{eff(inter)}} \quad (6)$$

where C_F and $C_{II(inter)}$ are the concentrations of free and intermolecularly bound hydroxyl groups, respectively, and $C_{eff(inter)}$ is the effective local concentration of oxygen atoms of the neighboring molecules near a given OH group. Since this form of intermolecularly bound hydroxyl absorbs in the same region of the spectrum (band II) as larger in-

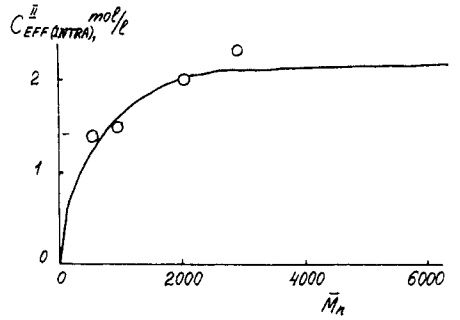


Figure 6. Experimental dependence of the effective local concentration of oxygen atoms of a given molecule close to the end hydroxyl group, $C_{eff(intra)}$, on PEG molecular weight. O are theoretical calculated values of $C_{eff(intra)}$.

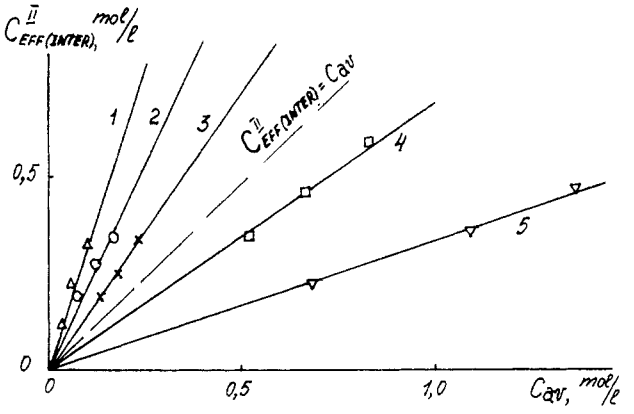


Figure 7. Dependence of the intermolecular effective local concentration of oxygen atoms, $C_{eff(inter)}$, on the average concentration of PEG solution per base-mole, C_{av}, for PEG with different molecular weights: (1) 300, (2) 600, (3) 1000, (4) 3000, (5) 6000.

tramolecular rings, its concentration $C_{II(inter)}$ is determined from the difference $C_{II(inter)} = C_{II} - C_{II(intra)} = C_{II} - K_2C_I$. It might be assumed that according to reaction 6 the constants, K_5, of the intermolecular HB formation do not depend on the length of the polymer chain and have the same values as K_M for the model system EME–DE. Under this assumption the values of $C_{eff(inter)}$ can be calculated. Their dependence on the average concentration C_{av} of the PEG solution calculated per base-mole for polymers with different molecular weights is represented in Figure 7. The direct proportionality of these values is obtained from the linear dependence between the ratio of the integral intensities of bands II and I, B_{II}/B_I, which can be represented as

$$\frac{B_{II}}{B_I} = \frac{A_{II}lC_{II}}{A_IlC_I} = \frac{A_{II}}{A_I}\frac{C_{II(intra)} + C_{II(inter)}}{C_I}$$

$$= \frac{A_{II}}{A_I}(K_2 + K_1K_5C_{eff(inter)})$$

and the total concentration of the PEG solution (Figure 6).

Since the experiments were carried out with dilute solutions, $C_{eff(inter)}$ is identical with C_{av} only under Θ-conditions. In a good solvent, where the molecules of the dissolved substances repulse, C_{av} is larger than $C_{eff(inter)}$, while in a bad solvent, where polymer molecules show a trend to association, C_{av} is smaller than $C_{eff(inter)}$. In other words, the ratio $C_{eff(inter)}/C_{av}$ in a dilute solution characterizes the thermodynamic quality of the solvent. Figure 8 shows that CCl_4 at 30 °C is a good solvent for PEG with molecular weight higher than 2300, while it is a bad solvent for PEG

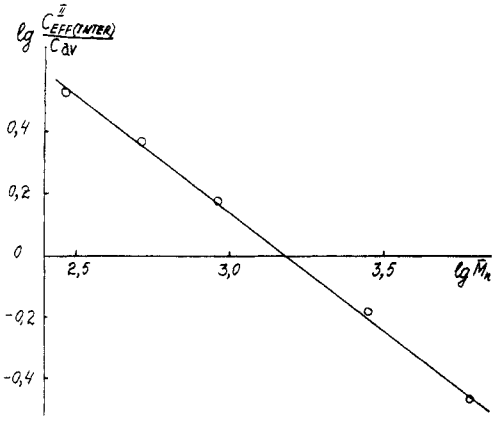


Figure 8. Dependence of the logarithm of the ratio between the effective and average concentrations for ether groups in solution on the logarithm of PEG molecular weight.

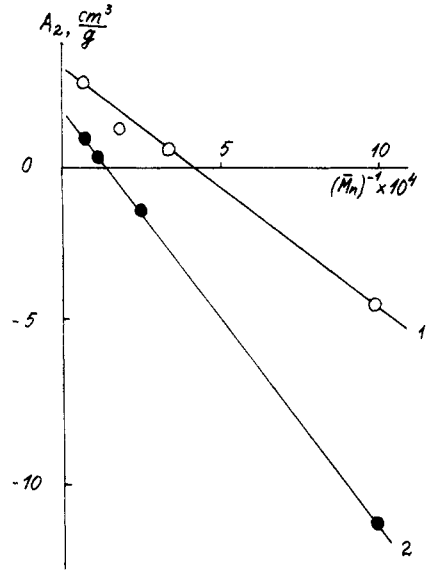


Figure 9. Dependence of the second virial coefficient A_2 for PEG solutions in CCl_4 at 30.2 °C (1) and in benzene at 32.2 °C, (2) (data from ref 1) on the inverse value of PEG molecular weight.

with molecular weight lower than 2300.

A change in the sign of the second virial coefficient A_2 and hence a change in the thermodynamic quality of the solvent with increasing length of the polymer chain in CCl_4 has also been shown independently by osmometry (Figure 9). The correlation between the results of both methods is good and they predict the fulfilled Θ-conditions at 30 °C for PEG with molecular weight of ~2300 (Figure 8 and 9). A similar dependence of A_2 on the chain length was previously obtained for PEG solutions in benzene[1] (Figure 9). The observed change in the thermodynamic quality of the solvent with increasing molecular weight is, probably, caused by the simultaneous action of two factors: attraction between the OH group of one molecule and the ether oxygen atoms of other molecules and repulsion between oxygen atoms of different molecules. Attraction dominates for short polymers and they tend to associate. In this case the solvent is bad. For high molecular weight PEG with long sequences of oxygen atoms repulsion dominates and the solvent is good for these polymers.

Let us consider the regularities of intermolecular interactions of PEG end groups proceeding according to the scheme

$$2{\sim}OCH_2CH_2OH \overset{K_6}{\rightleftharpoons} \begin{matrix}{\sim}OCH_2CH_2OH \\ \vdots \\ HOCH_2CH_2O{\sim}\end{matrix} \qquad K_6 = \frac{C_{III(inter)}}{C_F^2} \qquad (7)$$

where C_F is the concentration of free hydroxyl groups, and $C_{III(inter)}$ is the concentration of PEG dimers with intermolecular HBs in a 10-membered ring. This type of interaction, in addition to the corresponding intramolecular H complexes, is exhibited in band III of the PEG spectrum. Therefore, the concentration $C_{III(inter)}$ is found by subtraction, $C_{III(inter)} = C_{III} - C_{III(intra)} = C_{III} - K_3C_I$, which gives the possibility of calculating the constants K_6 from formula 7. The values of K_6 are represented in Table III. It is seen that as one could expect the values of K_6 do not depend on the molecular weight of PEG.

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References and Notes

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